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(54) Title: A STEAM REFORMING CATALYST AND PROCESS FOR PRODUCTION THEREOF

(57) Abstract

A steam reforming catalyst and process for production thereof wherein the catalyst includes from about 50 to about 75 percent nickel oxide, from about 5 to about 12 percent of an alkaline earth oxide, from about 10 to about 40 percent of a support material and from about 4 to about 20 percent of a rare earth oxide promoter.

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Title

A STEAM REFORMING CATALYST AND PROCESS FOR PRODUCTION THEREOF

Field of Invention

This invention relates to an improved catalyst for steam reforming hydrocarbon products and a process for preparing that catalyst.

Prior Art

Production of methane containing gases such as town gas by reacting steam and C_2-C_{10} hydrocarbons has been practiced for more than 50 years. Pre-reforming technology has gained universal acceptance as a means of solving problems associated with tubular steam reforming at elevated temperatures (550-850°C). Severe coking of the catalyst necessitates frequent shut down in commercially operating plants. Therefore, in recent years, an adiabatic pre-reforming system is introduced to safeguard the tubular reforming process and to decrease the carbon formation in primary reforming catalysts. Pre-reforming catalysts are operating at lower temperatures (400-500°C) and low steam to carbon ratio. Since most of the catalyst poisons are removed in the pre-reformer bed, overall efficiency of downstream process is improved. Further, it results in good improvement in process economy.

A survey of patent literature indicates that a combination of nickel oxide and various promoters on

different supports have been extensively investigated for low temperature steam-naphtha reforming. A lanthanide rare earth promoter was used in U.S. Patent No. 3,404,100 in a coprecipitated Ni/Al_2O_3 catalyst for reforming in the temperature range 320-480°C. A methane rich gas process using a combination of NiO, CuO, Cr_2O_3, MnO and SiO_2 for operations at temperatures as low as 300-325°C has been described in U.S. Patent No. 3,429,860. A catalytic gas process has been described in German Offen. 230,628, using potash promoted Ni/Al_2O_3 catalyst operating at 430-450°C and steam to carbon ratio of 1.6. Lanthana or ceria promoted Ni/Al_2O_3 catalysts were prepared for the synthesis of methane containing gases by the decomposition of steam and C_2-C_{12} hydrocarbon in the temperature in the range 300-550°C in German Offen. 2,739,466.

Steam reforming is often accompanied by carbon forming reactions and therefore Ni catalysts have to be supported on suitable materials so as to achieve an equilibrium between carbon formation and carbon removal under operating conditions. It is very difficult to achieve this condition since Ni catalysts are sensitive to changes in feed composition. Hence the choice of a suitable support which could resist carbon formation is preferred.

Objects of the Invention

An object of this invention is an improved catalyst for producing methane rich gases via hydrocarbon steam reforming and a process for the preparation of said catalyst having an advantageous application for producing methane rich gases.

Another object of this invention is an improved catalyst for producing methane rich gases and a process for its preparation, said catalyst having a high activity, selectivity and stability even at high hydrocarbon space velocity, low temperature and low steam to hydrocarbon ratio.

Still another object of this invention is an improved catalyst for producing methane rich gases and a process for its preparation, said catalyst having high nickel dispersion.

Yet another object of this invention is an improved catalyst for producing methane rich gases and a process for its preparation, said catalyst having high reducibility properties.

A further object of this invention is an improved catalyst for producing methane rich gases and a process for its preparation, said catalyst having high coke resistance properties.

Further objects and advantages of this invention will

be more apparent from the ensuing description.

Brief Description of the Invention

According to this invention there is provided a novel catalyst and a process for preparing an improved catalyst suitable for producing methane rich gases via hydrocarbon steam reforming comprising reacting an aqueous solution of metal nitrates with an aqueous alkali solution containing silica and alumina to form a mixed precipitated slurry, washing and drying the said precipitate and calcining the said precipitate.

A number of catalysts are prepared by reacting together salts of nickel and lanthanides with alkali solution over alumina/silica/magnesia supports at temperatures ranging from ambient to 85°C and at variable pH of 7-10. The precipitate is aged at ambient to 85°C for 1 to 10 h. The precipitated slurry is washed with DM (demineralized) water at 40-80°C to reduce sodium and sulfur content to less than 100 ppm. The slurry is filtered and the cake is dried in a band/box dryer at 350-550°C to control the loss on ignition to between 3-10 percent. The oxide is mixmulled with DM water and graphite (1 to 3 percent) and dried at 100-200°C to control loss on ignition to between 4-13 percent. It is further granulated over a 12-100 sieve and tabletted or extruded in cylindrical shapes. Finally, it is calcined at

350-550°C.

The catalysts thus prepared have a composition within the range as given below:

	percent by wt.
NiO	50-75
MgO	5-12
Al_2O_3	7-15
SiO_2	2-23
Lanthanide oxides	4-18

The catalyst prepared by the process of this invention has a surface area of 160-250 m^2/g, a total pore volume of 0.18 to 0.30 ml/g with mesopores constituting between 20 to 40 percent of the total pore volume, and a bulk density of 0.8 to 1.2 g/ml.

The following metal salt solutions are used for the preparation of 1 kg. of all the catalysts.

Solution I 2500g of $Ni(NO_3)_2.6H_2O$ in 10L of DI (deionized) water

Solution II 200g $Ce(NO_3)_3.6H_2O$ in 1 L DI water

Solution III 200g $La(NO_3)_3.6H_2O$ in 1 DI water

Solution IV 300g $Mg(NO_3)_2.6H_2O$ in 1 L DI water

Solution V 2200g Sodium Carbonate (Technical grade-85% purity) in 10 L DI water

The following supports were also used for the preparation of catalyst samples.

1. Silica containing 80% SiO_2 and rest H_2O

2. Activated alumina containing 70% Al_2O_3 (micronised to particle size < 1m) and the rest H_2O

3. Activated magnesia containing 85% MgO and the rest H_2O/CO_2

Example A

A mixture of Solutions I, II and III was slurried with 50g precipitated silica, 60g activated magnesia and 150g activated alumina, which were slurried in Solution V. The final pH of the mixture was 8-9 and the temperature during precipitation was maintained in the range 40-80°C. The precursor obtained was processed to a finished product after washing, drying, mixmulling, granulation, tabletting and final calcination. A decreased interaction of the active phase with the support leads to an improved reducibility of nickel oxide.

Example B

This catalyst preparation was very similar to Example A, except that the supports used (silica, magnesia and alumina) were hydrothermally treated before being taken for precipitation. Hydrothermal treatment of the supports were carried out in a steam autoclave at 200-220°C for 16 b. This method yields a catalyst which could impart extra stability for the support. Support provides a very vital role in providing the reaction sites for the chemisorption of steam

during naphtha reforming.

Example C

Catalyst prepared by methods A and B were analyzed several times and the composition was as follows:

$NiO/Al_2O_3/MgO/SiO_2/La_2O_3/CeO_2$ 65/10/5/4/8/8

Method of preparation of reference catalyst R

Reference catalyst R was prepared following the technique described in U.S. patent No. 3,404,100. 1500g $Ni(NO_3)_2 6H_2O$ and 1480g $Al(NO_3)_3.6H_2O$ was dissolved in 6 L DI water, stirred and the solution was brought to 50°C. Then, 2080g NH_4HCO_3 were added with stirring maintaining the slurry at 50°C. The slurry was filtered and washed. To the resultant precipitate was added 123g each of lanthanum nitrate and 61.5g cerium nitrate dissolved in a little deionized water. The catalyst thus prepared was dried overnight at 110°C and calcined for 4 h at 400°C.

Evaluation results No. 1

The catalyst of methods A and B and the reference catalyst R were evaluated for naphtha steam reforming activity in a high pressure flow reactor after reducing 50cc of the catalyst with hydrogen at 400°C for 18 h at a space velocity of $2000h^{-1}$ and at atmospheric pressure and further reduction at 18 atm for 2 h. Reaction was carried out with steam to naphtha weight ratio of 2:5 at 380-420°C and 18

kg/cm^2 pressure. The product gas contains 0.1-0.6% CO, 20-24% CO_2, 58-64% methane and the balance hydrogen. No naphtha slip was observed while testing for 50 hrs. for all the catalysts.

Evaluation Result No. 2

All the catalysts were evaluated as per the test conditions in evaluation No.1 except that steam to naphtha wt. ratio was reduced to 1.5. Testing at this low S/C ratio indicated the extent of carbon deposition in the following order: R>A and B. No naphtha slip was observed.

Evaluation Result No. 3

For catalysts A and B silica was estimated in the condensate collected after testing as per evaluation in 1 and 2. Percent silica migrated in both cases was found to be in the range 0.002 to 0.0025 which indicates that silica migration is negligible for the catalysts of the present invention.

Evaluation Result No. 4

The test conditions were maintained identical to Evaluation No. 2 except that the operating temperature was lowered to 340°C when traces of naphtha was observed in the condensate. No naphtha slip was observed for all the catalysts up to 340°C.

Evaluation Result No. 5

The test conditions were maintained similar to Evaluation No. 1 except that the aromatic content in the feed stock was varied from 10-60%. No naphtha slip was observed up to 40% aromatics in the feed while testing for 20 hrs. duration. However, at 60% aromatics in the feed, naphtha slip was observed in the range 6 to 8% and the following trend was observed: R > A and B.

Evaluation Result No. 6

Effect of higher feed rates of hydrocarbon was particularly studied for catalysts A and B in comparison to the reference catalyst R. The catalysts were tested at a high naphtha space velocity of 8.0, operating temperature 450°C and pressure maintained at 10kg/cm^2. Lined out naphtha slip after 8 hours run for catalysts A, B and R are 33%, 36% and 37%. Hence activity for these catalysts at higher space velocities shows the following trend: A is greater than B and approximately equal to R.

Evaluation Result No. 7

Physical integrity of the catalysts were evaluated by subjecting the catalysts to various high temperature/hydrothermal treatments. The catalysts were heated to 500°C and plunged in cold water. Maximum retained crush strength (83%) was observed for catalyst A. Further,

crush strength was determined after refluxing the catalysts in water for 2h. In both the cases, the percent retained crush strength was in the order A and B > R. The discharged catalysts, after activity evaluation, also showed the same trend in percentage retained crush strength. Percentage surface area loss on subjecting the catalysts to thermal/hydrothermal treatments or after test run was also found to be minimum for catalyst A (24-35%).

Evaluation Result No. 8

Acidity determinations were carried out by NH^3-TPD. Acidity of catalysts A and B are comparable and lower than that of the reference catalyst R. Further, compared to catalyst R, the ammonia desorption is higher at lower temperatures for catalysts A and B. Strength of acid sites responsible for carbon deposition are lower for A and B compared to catalyst R.

Evaluation Result No. 9

The nickel dispersion (%) as well as percent nickel reducibility were evaluated and are found to be maximum for catalyst C. The dispersion follows the trend A and B > R and percent reducibility follows the order: A and B > R.

We Claim

1. A steam reforming catalyst comprising from about 50 to about 75 percent of a nickel oxide, from about 5 to about 12 percent of an alkaline earth oxide, from about 10 to about 40 percent of a support material and from about 4 to about 20 percent of a rare earth oxide promoter.

2. The steam reforming catalyst of Claim 1 wherein the support material is selected from the group consisting of alumina, silica, magnesia and mixtures thereof.

3. The steam reforming catalyst of Claim 1 wherein the rare earth oxide promoter is selected from the group consisting of an oxide of cerium, an oxide of lanthanum and mixture thereof.

4. The steam reforming catalyst of Claim 1 wherein the rare earth oxide promoter comprises an oxide of cerium and an oxide of lanthanum.

5. The steam reforming catalyst of Claim 1 wherein the alkaline earth oxide comprises magnesium oxide.

6. The steam reforming catalyst of Claim 1 wherein the support material comprises a combination of silica and alumina.

7. The steam reforming catalyst of Claim 1 comprising a surface area from about 160 to about 250 m^2/g.

8. The steam reforming catalyst of Claim 1 comprising

a pore volume is from about 0.18 to about 0.30 ml/g.

9. The steam reforming catalyst of Claim 1 comprising about 20 to about 40 percent of its pores in the mesopore range.

10. The steam reforming catalyst of Claim 1 comprising a bulk density of about 0.8 to about 1.2 g/ml.

11. A steam reforming catalyst comprising from about 50 to about 75 percent of a nickel oxide, from about 5 to about 12 percent of an alkaline earth oxide, from about 10 to about 40 percent of a support material and from about 4 to about 20 percent of a rare earth oxide promoter, selected from the group consisting of an oxide of lanthanum and an oxide of cerium and mixtures thereof.

12. The steam reforming catalyst of Claim 11 wherein the support material is selected from the group consisting of alumina, silica, magnesia and mixtures thereof.

13. The steam reforming catalyst of Claim 11 wherein the support material comprises a mixture of silica and alumina.

14. The steam reforming catalyst of Claim 11 wherein the alkaline earth oxide comprises magnesium oxide.

15. A steam reforming catalyst comprising from about 50 to about 75 percent of an oxide of nickel, from about 5 to about 12 percent of an alkaline earth oxide, from about

10 to about 40 percent of a support material selected from the group consisting of silica and alumina and mixtures thereof and about 4 to about 20 percent of a rare earth oxide promoter.

16. The steam reforming catalyst of Claim 15 wherein the rare earth oxide comprises an oxide of cerium, an oxide of lanthanum or combinations thereof.

17. The steam reforming catalyst of Claim 15 wherein the rare earth oxide comprises an oxide of cerium and an oxide of lanthanum.

18. The steam reforming catalyst of Claim 15 wherein the alkaline earth oxide comprises magnesium oxide.

19. A steam reforming catalyst comprising from about 50 to about 75 percent of a nickel oxide, from about 5 to about 12 percent of an alkaline earth oxide, from about 10 to about 40 percent of a support material selected from the group consisting of silica, alumina and mixtures thereof and from about 4 to about 20 percent of a rare earth oxide promoter selected from the group consisting of an oxide of cerium, an oxide of lanthanum and mixtures thereof.

20. The steam reforming catalyst of Claim 19 wherein the alkaline earth oxide comprises magnesium oxide.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J23/83 C01B3/40 C10G11/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J C01B C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 469 815 A (SAMBROOK RODNEY M ET AL) 4 September 1984 see the whole document	1-20
X	EP 0 033 505 A (KELLOGG M W CO) 12 August 1981 see claims 1-17	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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